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AFRPL-TR-68-235

**DEVELOPMENT OF A LOW COST
CATALYST FOR HYDRAZINE (U)**

**QUARTERLY PROGRESS REPORT NO. 3
SEPTEMBER 15, 1968 - DECEMBER 15, 1968**

by

**William F. Taylor
Martin Lieberman
Murray S. Cohen**

JAN 15 1969

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Prepared under Contract No. F04611-68-C-0044 for

**Air Force Rocket Propulsion Laboratory
Edwards Air Force Base
Edwards, California 93523**

Esso Report No. GR-3-DCH-68

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DEVELOPMENT OF A
LOW-COST CATALYST FOR HYDRAZINE (U)

By

William F. Taylor
Martin Lieberman
Murray S. Cohen

Third Quarterly Report
September 15, 1968 - December 15, 1968
Contract No. F04611-68-C-0044

For

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I. (C) INTRODUCTION (U)

(U) The object of the work conducted under this contract is to develop a low cost, readily available, active catalyst for the decomposition of hydrazine. At the present time, an active, spontaneous catalyst does exist for the decomposition of hydrazine, this is Shell 405. However, it derives its activity from the precious metal iridium which is very costly (\$2,000/lb) and limited in availability. In applications requiring a large number of monopropellant engines, and hence large catalyst quantities, a reliable, low cost readily available hydrazine decomposition catalyst is required.

(U) This report describes the work conducted during the second quarter of this contract. Our effort, during this period, has been primarily devoted to the investigation of cobalt-ruthenium hybrid catalysts and ruthenium catalysts, both using alumina support structures.

(C) The use of ruthenium in cobalt-ruthenium hybrid catalysts effected a significant reduction in catalyst ignition delay when compared with cobalt catalysts containing no ruthenium. However, ruthenium on an alumina support, containing no cobalt, was significantly more active than the cobalt-ruthenium hybrid structures; ignition delay performance of alumina supported ruthenium catalysts approached the performance of Shell 405.

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II. (C) TECHNICAL PROGRAM (U)

A. (C) CATALYST ISOTHERMAL EVALUATION (U)

(U) The basic information required to satisfactorily define the performance of a hydrazine decomposition catalyst include the isothermal low-temperature activity, the apparent activation energy for the decomposition process, and the ignition delay of the adiabatic catalyst bed. The latter is determined, in part, by the first two of these performance parameters. Isothermal low temperature activity and apparent activation energy for the decomposition process are obtained by means of the gas evolution rate resulting from hydrazine decomposition in the isothermal test apparatus. This apparatus is described in our first Quarterly progress report.

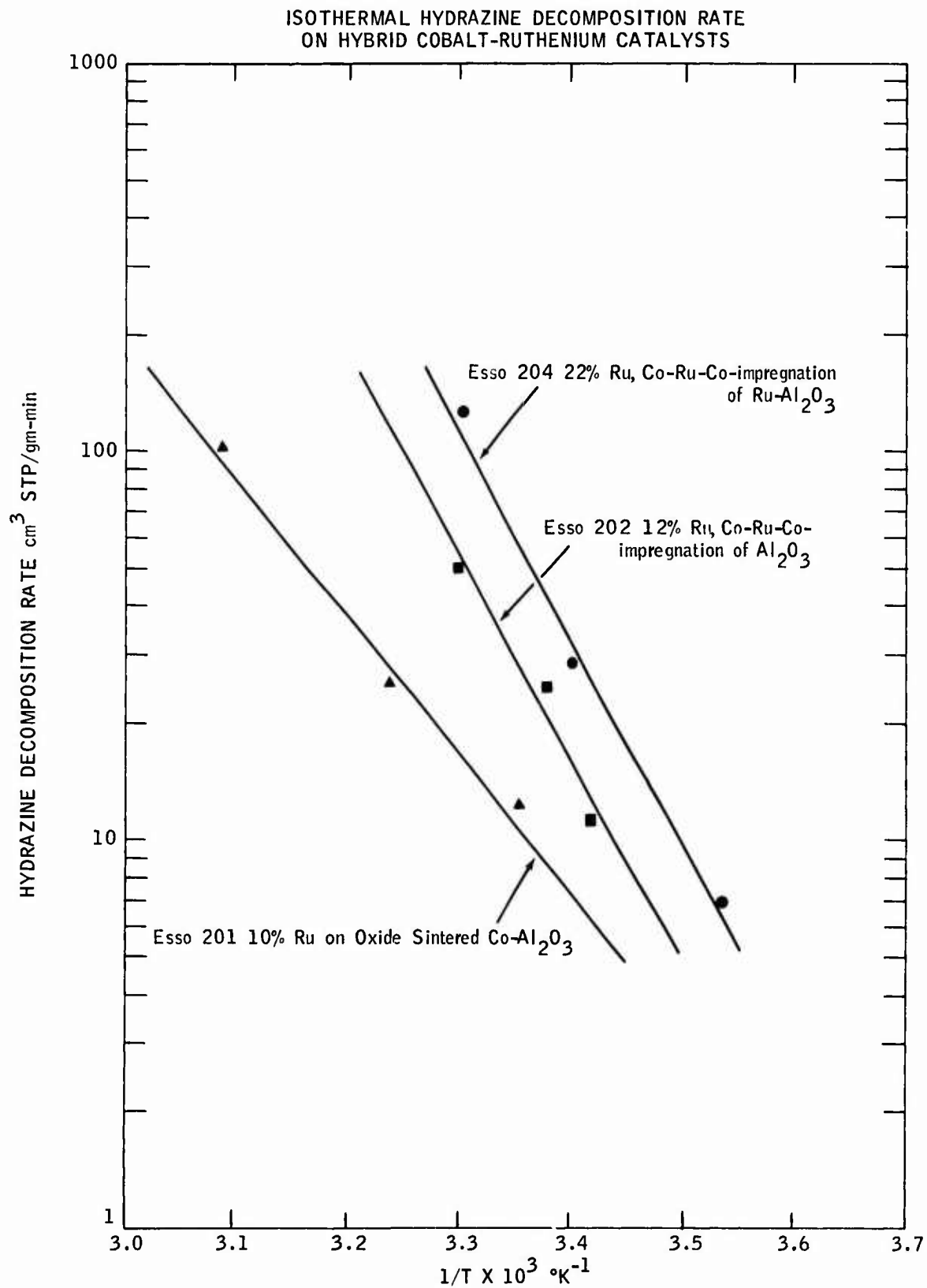
1. (C) Cobalt-Ruthenium Hybrid Catalysts (U)

(C) The incorporation of readily reduced transition metals into our cobalt catalyst formulation have improved the low temperature activity and ignition delay of the cobalt catalyst system. Data presented in our second Quarterly report indicated that the incorporation of low concentrations of platinum and palladium into alumina supported cobalt preparations improved the isothermal activity and ignition delay of Esso 101 type catalysts. During the past quarter, this work has extended to ruthenium-cobalt hybrid catalysts. Ruthenium is a particularly attractive transition metal to work with because of its wide availability and reasonable cost. Proprietary information recently made available to Esso Research and Engineering Co., indicated that there is about 150,000 troy ounces of ruthenium/year available, primarily from two sources: the Johnson Matthey and Co. (as a by-product of gold and platinum refining) and the international Nickel Co. (as a by-product of copper and nickel refining). There is also believed to be a substantial backlog of this metal presently available.

(C) Several ruthenium-cobalt-alumina catalysts were prepared by different fabrication techniques. These include 10% ruthenium on oxide sintered cobalt-alumina (prepared by co-precipitation), Esso 201; a structure consisting of 12% ruthenium prepared by co-impregnation of alumina with cobalt ruthenium solution, Esso 202; a structure consisting of 22% ruthenium prepared by co-impregnating a ruthenium on alumina support with cobalt ruthenium solution, Esso 204. The results of the isothermal hydrazine decomposition tests, using these structures, are presented in Table I and Figure 1.

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FIGURE 1



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TABLE I

(C) ISOTHERMAL DECOMPOSITION RATE OF
COBALT-RUTHENIUM HYBRID CATALYSTS (U)

Catalyst	Description	Hydrazine Decomposition Rate at 23°C cm ³ STP/gm-min	Apparent Activation Energy Kcals/gm-mole
Esso 201	10% Ru, 75% Co on oxide sintered cobalt-alumina	10	19
Esso 202	12% Ru, 33% Co co-impregnated alumina	25	24
Esso 204	22% Ru, 33% Co co- impregnated Ru-alumina	50	24
Esso 203	12% Ru, 33% Co, 55% Alumina co-precipitated	15	24
Esso 101	70% Co, 30% Alumina co-precipitated	75	26

(C) Several interesting observations may be made about the data in Table I and Figure 1. First, the isothermal hydrazine decomposition rate of the cobalt-ruthenium hybrid catalysts is less than that of the basic Esso 101 catalyst which contains no ruthenium. Surface area differences are believed to be partly responsible for this difference in activity. Surface area data, thus far obtained, indicate that the impregnated hybrid catalysts have considerably less surface area than the co-precipitated Esso 101 preparation. However, the magnitude of this surface area difference cannot possibly account for the entire activity difference observed. For instance, Esso 201 has about one half the surface area of Esso 101 with comparable cobalt loadings. Yet, the isothermal activity of the Esso 101 catalyst is about seven times greater. This implies that a negative synergistic effect exists for the cobalt-ruthenium catalyst system. Further evidence of this is seen in a subsequent section on the evaluation of ruthenium-alumina catalysts. Despite the poor isothermal decomposition rate exhibited by the ruthenium-cobalt hybrid catalyst preparations, we felt it was important to pursue evaluation of these catalysts in motor firing studies. We believed that significant improvements in ignition delay might still be seen with hybrid catalysts having appreciable noble metal area, not affected by densitization procedures. This hypothesis was confirmed in subsequent motor firing studies discussed in another section of this report.

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(C) The performance of cobalt ruthenium hybrid catalysts appears to be dependent on the fabrication procedure. Esso 202 and 203 have the same component formulation but different isothermal activity. Surface area differences resulting from different fabrication techniques is held to be a contributing factor. Measurements now being made will indicate the extent of this contribution. The lower apparent activation energy of Esso 201 compared with other hybrid catalyst preparation is probably also a result of fabrication differences. One possible explanation for this lower activation energy is the increased pore diffusional contribution resulting from the presintering of the substrate used on Esso 201. This oxide sinter strengthening technique is discussed in a subsequent section of this report.

2. (C) Ruthenium Catalysts (U)

(C) A series of ruthenium on alumina catalysts were prepared to determine whether performance could be improved by removing the cobalt from the system. The effect of ruthenium concentration, catalyst support type, as well as the addition of platinum, on catalyst isothermal hydrazine decomposition activity was studied. The results are presented in Table II and Figure 2 and discussed in the following paragraphs.

TABLE II

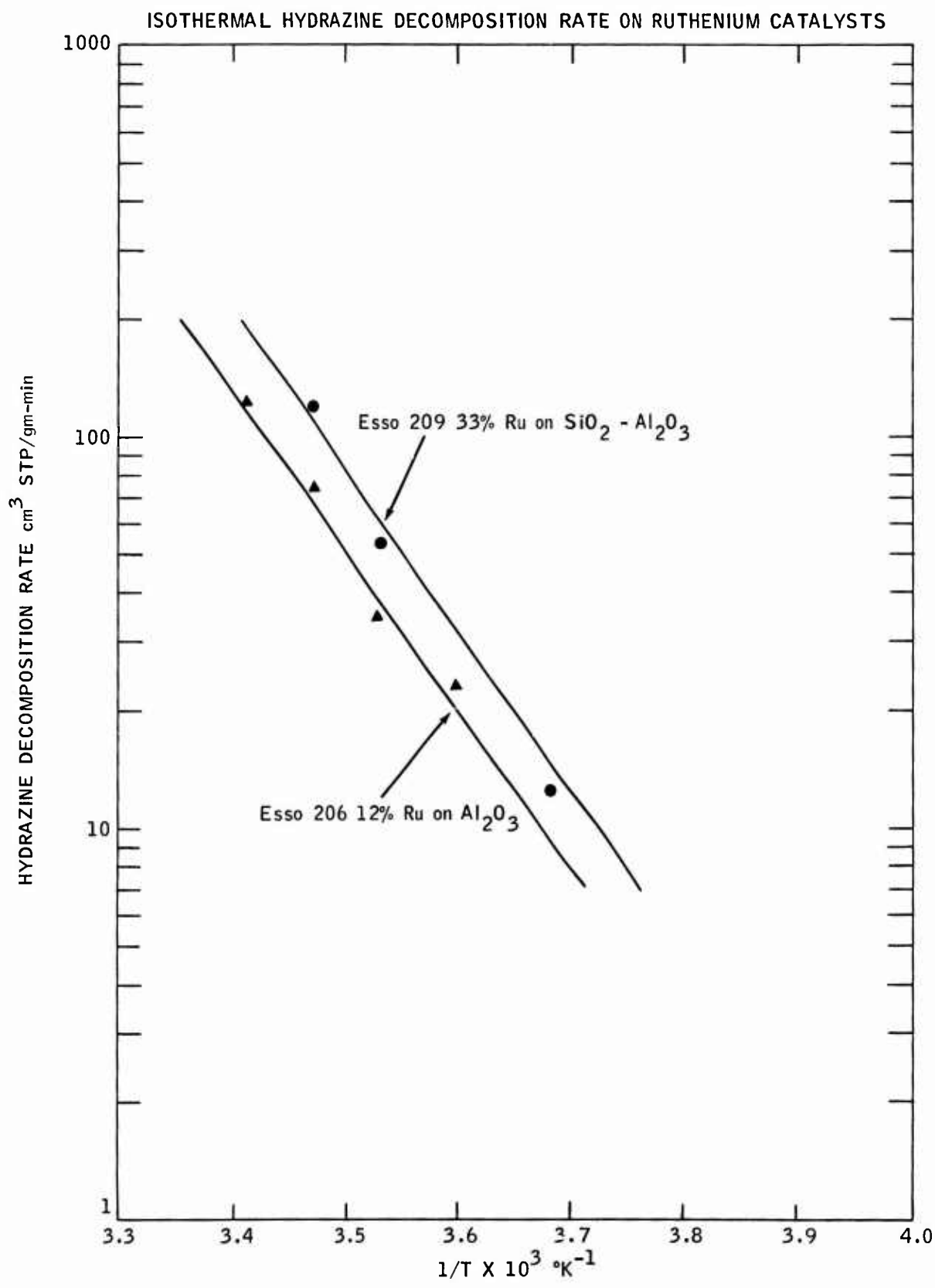
(C) ISOTHERMAL HYDRAZINE DECOMPOSITION RATE
ON RUTHENIUM CATALYSTS (U)

Catalyst	Description	Hydrazine Decomposition Rate at 23°C cm ³ STP/gm-min	Apparent Activation Energy Kcals/gm-mole
Esso 206	12% Ru on Alumina	170	19
Esso 207	23% Ru on Alumina	200	19
Esso 208	36% Ru on Alumina	360	19
Esso 209	33% Ru on Silica- Alumina (6% SiO ₂)	280	19
Esso 210	5% Pt, 33% Ru on Alumina	359	Not Measured

(C) Catalyst isothermal activity increases with ruthenium metal concentration and is more than 5 times as active as Esso 101 at the 36% ruthenium level. The cobalt free, 12% ruthenium on alumina, catalyst was far more active than any of the cobalt-ruthenium hybrids having the same ruthenium content. This data further supports the fact that there is negative synergistic effect exhibited by cobalt-ruthenium hybrid catalysts toward hydrazine decomposition and that the performance of a ruthenium catalyst depends on the nature of the support used in the fabrication. The relative performance

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FIGURE 2



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of ruthenium-alumina and cobalt-ruthenium-alumina catalysts in the motor firing studies yields the same conclusion. The isothermal data suggest that higher ruthenium levels would yield more active catalysts. However, measurements made in the 5 lb. thrust engine indicate that there is a leveling off in the ignition delay as the 35% ruthenium content is approached. Catalyst bed startup performance is discussed in another section of this report. The activation energy of ruthenium alumina catalysts is lower than that of the cobalt-ruthenium-alumina hybrids. The hybrids would thus be more active above 200°C. However, at the adiabatic firing temperature, the reactivity of the catalyst is undoubtedly diffusion limited. The apparent activation energy of the catalysts would then be primarily controlled by pore diffusion effects.

(C) The use of a silica-alumina support (Harshaw 1602) does not appear to offer any great advantage over alumina in terms of isothermal activity. Little advantage of this support is also seen in the motor firing studies. The incorporation of 5% platinum into the formulation by co-impregnation appeared to improve the isothermal activity. This improvement was reflected in a very short ignition delay during the first firing of this catalyst in the 5 lb. thruster. However, this activity was lost in subsequent 5 lb. thrust motor firings. Motor firing performance of these catalysts is presented in the following paragraphs. Complete data is presented in the Appendix.

B. (C) CATALYST MOTOR FIRING EVALUATION (U)

(U) Evaluation of a hydrazine decomposition catalyst in an actual monopropellant catalyst engine is required to completely characterize its start-up behavior, steady-state performance and life. In the isothermal test, catalyst powder is used in a well stirred dilute suspension in liquid hydrazine. Both mass and heat transfer effects are not important. However, in an actual motor firing of a bed of catalyst pellets, the system approaches adiabatic conditions with a very rapid rise in temperature and pressure. Heat and mass transfer, particularly pore diffusion, become important. Furthermore, large internal pressures are built up within the catalyst pores putting a severe strain on the pellet structure. A series of tests were performed using a 5 lb. thrust static rocket engine. The ignition delay of several cobalt-ruthenium hybrid and ruthenium catalysts was measured at various bed temperatures. The results of these tests are presented in the following paragraphs.

1. (C) Cobalt-Ruthenium Hybrid Catalysts (U)

(C) The ignition delay of cobalt-ruthenium hybrid catalysts using hydrazine fuel was measured at several catalyst bed temperature levels. Catalyst pellets 1/8"D x 1/8"L were used in all cases. The results of these studies are presented in Table III and Figure 3. Complete engine data are given in the Appendix.

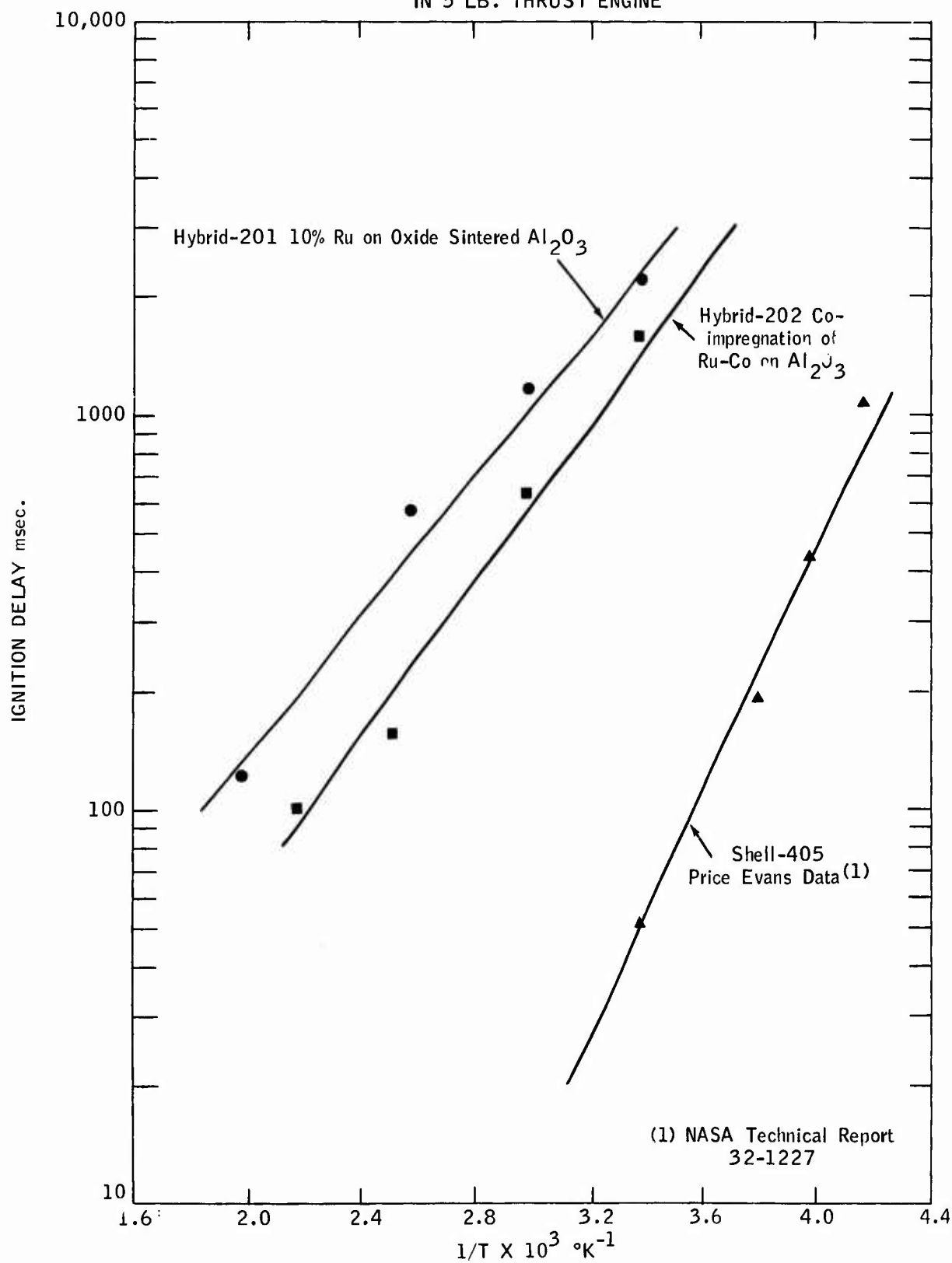
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FIGURE 3

PERFORMANCE OF COBALT-RUTHENIUM-HYBRID CATALYSTS
IN 5 LB. THRUST ENGINE



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TABLE III

(C) IGNITION DELAY OF COBALT-RUTHENIUM
HYBRID CATALYSTS (U)

Catalyst	Description	Ignition Delay at 23°C msec.
Esso 101	70% Co, 30% Alumina co-precipitated	>6,000
Esso 202	12% Ru, 33% Co co-impregnated alumina	1,500
Esso 201	10% Ru, 75% Co on oxide sintered cobalt alumina	2,000
Esso 200	12% Ru on cobalt impregnated alumina	750

(C) The incorporation of ruthenium into cobalt-alumina catalyst formulations is seen to dramatically reduce the ignition delay. Furthermore, the degree to which the ignition delay is reduced depends on the mode of preparation of the catalyst. Catalysts 202, 201 and 200 all have approximately the same ruthenium content, but differ in fabrication technique. Esso 200 was prepared by first depositing the cobalt on an alumina support and then depositing the ruthenium on top of the cobalt. In this case, maximum availability of the ruthenium surface was probably achieved. Esso 202 utilized a co-impregnation of cobalt and ruthenium salts. This technique probably resulted in less available ruthenium surface. Esso 201 utilized a ruthenium impregnation of a cobalt alumina support and, thus, should also have readily available ruthenium metal surface. However, the cobalt alumina support was presintered yielding a support with about one half the surface area of Esso 200. This support surface area difference is a possible explanation of the longer ignition delay of Esso 201 in comparison to Esso 200. Despite the significant improvement in ignition delay resulting from the use of ruthenium in cobalt-ruthenium hybrids, performance had not approached that of Shell 405. Emphasis was thus shifted to the more promising ruthenium on alumina catalysts.

2. (C) Ruthenium Catalysts (U)

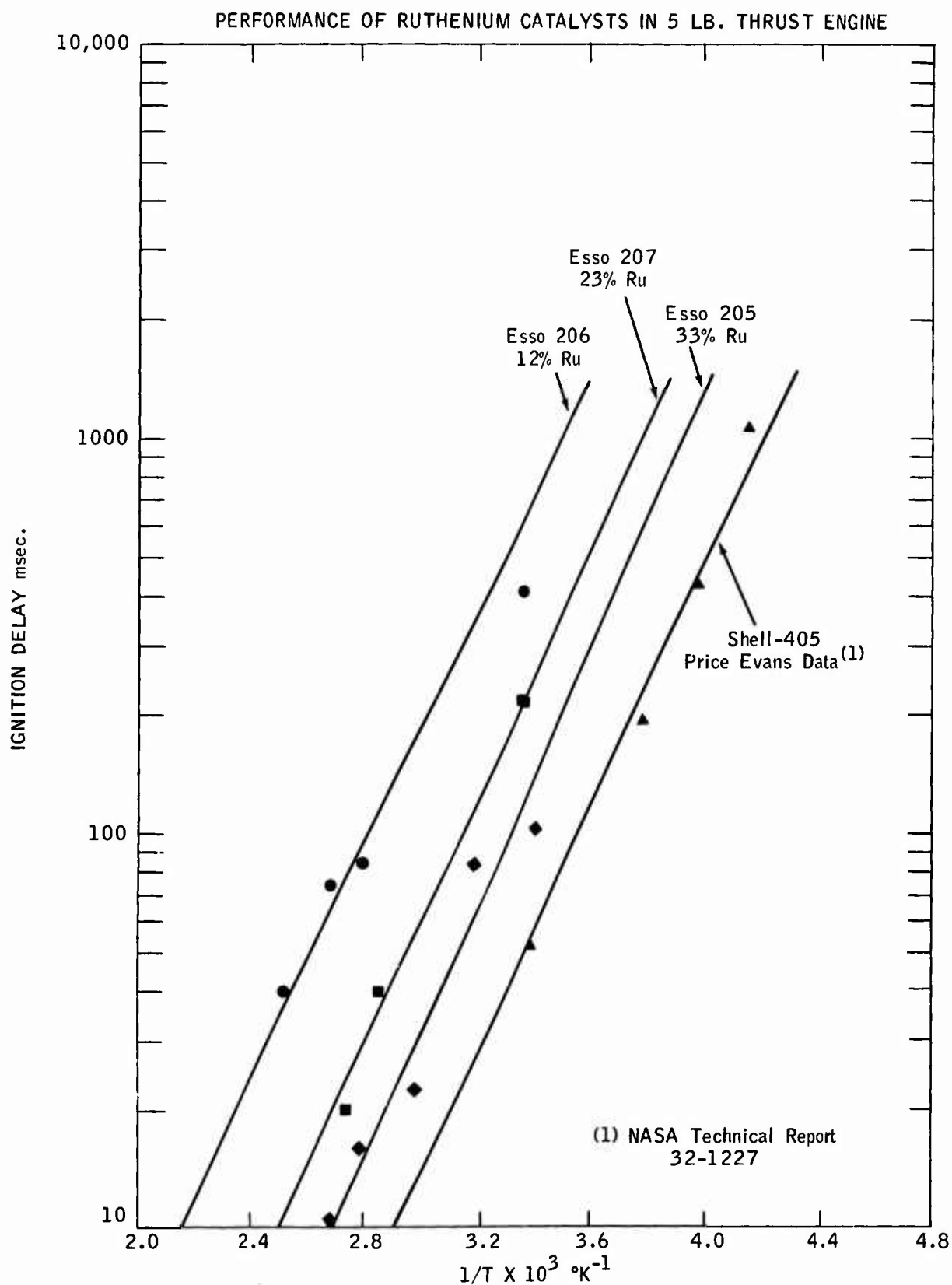
(C) The high low temperature activity of cobalt free ruthenium on alumina catalysts appears as a significant reduction in ignition delay. Tests on 1/8"D x 1/8"L pellets fabricated by ruthenium salt impregnation of preformed Harshaw 1404 alumina gave engine start-up performance which approached that of Shell 405. The results of these tests are presented in Table IV and Figure 4 and discussed in the following paragraphs.

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FIGURE 4



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TABLE IV

(C) IGNITION DELAY OF RUTHENIUM CATALYSTS
IN 5 LB. THRUST ENGINE (U)

Catalyst	Description	Ignition Delay at 23°C msec.
Esso 205	33% Ru on Alumina	120
Esso 206	12% Ru on Alumina	620
Esso 207	23% Ru on Alumina	220
Esso 209	33% Ru on Silica-Alumina 6% Silica	100
Esso 210	5% Pt, 33% Ru on Alumina	5 (first firing) 100

(C) The ignition delay is seen to depend on the ruthenium concentration, decreasing as the catalyst ruthenium content increases. The incremental reduction in ignition delay in going from 23 to 33% ruthenium is much less than that in going from 12 to 23%. Preliminary data on a higher ruthenium concentration catalyst further indicates a leveling off of the ignition delay. Thus, very high ruthenium loadings (>50%) are not expected to result in any further significant reduction in ignition delay.

(C) The incorporation of 5% platinum, by means of the co-impregnation of platinum and ruthenium salts, produced a catalyst that showed a very short ignition delay for the first firing. However, subsequent firings did not show any advantage over the platinum free catalyst having a comparable ruthenium content. One possible explanation for the very short ignition delay observed during the first firing of the platinum ruthenium catalyst is the relative ease in which platinum oxide is reduced. All catalysts, prepared by hydrogen reduction, are subsequently exposed to air and, hence, have a thin oxide layer on the surface. This oxide, which is easily reduced, reacts with hydrazine in a bipropellant mode for a fraction of a second giving the system an extra "kick". Platinum oxide is easier to reduce than ruthenium oxide and hence may have accounted for the rapid start. The ignition delay during the first firing of platinum free ruthenium catalysts is usually lower than the next few subsequent firings. The difference, however, was not nearly as great as that observed with the ruthenium-platinum catalyst. Further evidence of surface oxide effects was obtained by re-admitting air into a catalyst bed at room temperature after it had been fired a number of times. A significant reduction in ignition delay, (usually about 50%) and ignition spike pressure was observed in each case in which air was admitted to the reactor bed. However, the shortened ignition delay effect is, again, only present for the initial firing after exposure to air.

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(C) The use of a Silica-Alumina support, having about 30% more surface area than the pure alumina support, did not result in any appreciable reduction in ignition delay. Results were essentially the same as those of the alumina supported catalyst with a comparable ruthenium content.

C. (U) CATALYST PILL DEVELOPMENT (U)

(U) The techniques investigated to improve catalyst pill strength include sinter strengthening, and the incorporation of refractory cements into co-precipitated catalyst preparations. We have continued our effort in these areas extending the sinter strengthening concept to oxide systems and exploring other refractory cements.

1. (U) Oxide Sinter Strengthening (U)

(U) In our second Quarterly report, we showed how significant increases in pellet strength could be effected by subjecting co-precipitated, cobalt-alumina catalyst pills to a sintering treatment in Argon. This gain in pill strength was, however, accompanied by a severe loss in surface area. Using the same concept, we decided to extend the sintering treatment to cobalt oxide-alumina pills. The hope was that the cobalt oxide would be less sensitive to sintering and that strength could be maintained with less surface area shrinkage. Data presented in Table V suggest that this was true.

TABLE V

(U) PROPERTIES OF OXIDE SINTER
STRENGTHENED CATALYST PELLETS (U)

Sintering Technique	Crush Strength lbs.	Sintered Pellet Surface Area ⁽¹⁾ m ² /gm
Cobalt-oxide-alumina substrate sintered 1050°C in air for 1 hour	28	40
Cobalt-alumina sintered 1050°C in Argon for 15 min	50	1.3

(1) Surface area and pill strength of oxide sintered pellets was measured after subsequent reduction to cobalt

(U) Cobalt-oxide-alumina sintered catalyst pills had about 30 times the surface area of the cobalt-metal-alumina pills when the two catalysts were compared in the as reduced form. Furthermore, a longer sintering time was used with the oxide sintered catalyst which indicates that more control can be exercised with the oxide sintering approach. Pill strength of the oxide sintered catalyst was lower, but still higher than the 20 lb. crush strength of Shell 405.

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(U) Oxide sinter strengthening was also applied to preformed Harshaw alumina pills. Table VI shows how preformed pellet strength can also be improved by this technique.

TABLE VI

(U) SINTER STRENGTHENING OF
HARSHAW 1404 PREFORMED ALUMINA PELLETS (U)

Sintering Conditions	Crush Strength lbs.	Surface Area m ² /gm
None	20	180
1000°C, 2 hrs.	28	100
780°C, 2 hrs.	28	143

(U) Modest improvements in crush strength were observed using this treatment. However, the important result appears to be a significant improvement in the substrate's ability to remain intact after metal impregnation and subsequent motor firing. Impregnated catalyst pellets prepared without this treatment quickly break up in adiabatic motor firing tests; catalysts prepared using presintered alumina remain intact for several firings. It appears as if substrate dimensional equilibration is required for stable metal-alumina catalyst pellets that must be subjected to severe thermal and pressure stresses.

2. (U) Refractory Cements (U)

(U) The co-precipitation catalyst fabrication approach requires an additional method of subsequently fabricating catalyst pellets. Cold pressing of the precipitated powder, alone, has been found to provide inadequate crush and bursting strength. Therefore, suitable binder materials that could provide the additional strength were sought. Several refractory cements were evaluated as candidate binder materials. These include calcium aluminate, Ceramacast-505, Saureisin preparations P-1, 7 and 8 and a special Esso lithium-sodium silicate cement developed in our coatings laboratories. Of all the preparations tested, using crush strength and actual adiabatic firing tests, only the Esso lithium-sodium silicate cement showed promise for reasonably long term catalyst stability. However, all cements are notably weak in tension and the general approach of forming catalyst pellets from co-precipitated catalyst powder and cement binders does not look attractive for the severe physical stresses encountered in hydrazine monopropellant catalyst systems.

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III. (C) SUMMARY (U)

(C) The use of ruthenium in cobalt-ruthenium hybrid catalysts resulted in a significant reduction in catalyst ignition delay over cobalt catalysts containing no ruthenium. However, ruthenium on an alumina support, containing no cobalt, was significantly more active than the cobalt ruthenium hybrid structures.

(C) Ignition delay performance of alumina supported ruthenium catalysts is a function of the ruthenium concentration and approaches the performance of Shell-405 at a ruthenium concentration of 33%. Preliminary data indicate that the activity levels off at 35% ruthenium and further significant reduction in ignition delay is not anticipated for higher ruthenium loadings.

(C) The use of a support sintering strengthening technique is an important step in the preparation of metal-alumina catalyst pills by the impregnation technique. The technique gives greater pellet cohesive strength which is required during motor firings.

(C) The oxide sinter strengthening technique of co-precipitated cobalt-alumina catalysts is more attractive than the metal sintering technique. Considerable less surface area loss results from the oxide sinter treatment with subsequent reduction to the active catalyst metal.

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APPENDIX A

(C) CATALYST FIRING DATA - 5 LB. THRUST ENGINE (U)

Catalyst No. 428-73
(Esso 200)

Description: 12% Ruthenium on 33% Cobalt
Impregnated Preformed 1404 1/8"
Alumina

	Run No.					
	1	2	3	4	5	6
Fuel Temp., °C	----- 24 -----					
Bed Start-up Temp. °C	24	24	60	70	60	60
Bed Inlet Steady Temp. °C	158	310	240	235	245	230
Bed Center Steady Temp. °C	158	300	760	915	915	915
Bed Inlet Steady Pressure, psig	0	spike	180	162	150	145
Bed Outlet Steady Pressure, psig	0	spike	115	115	115	122
Bed Pressure Drop, psi	--	--	65	47	35	23
Ignition Spike Pressure, psi	----- not recorded -----					
Ignition Delay msec.	4,000	7,800	1,000	500	400	700
Wt. % Catalyst Loss and Fines/Cold Start	----- 3.2 -----					
Pulse Duration, sec.	2	2	15	15	15	15
Remarks						

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-74
(Esso 201)

Description: 10% Ruthenium on CO-
Precipitated Oxide Sintered
Cobalt Alumina (75% Cobalt)

	Run No.							
	1	2	3	4	5	6	7	8
Fuel Temp., °C	----- 25 -----							
Bed Start-up Temp. °C	25	60	65	65	65	116	240	25
Bed Inlet Steady Temp. °C	375	510	220	850	900	235	240	205
Bed Center Steady Temp. °C	385	635	845	850	860	830	830	830
Bed Inlet Steady Pressure, psig	25	27	120	105	105	95	110	105
Bed Outlet Steady Pressure, psig	20	25	80	100	100	90	95	90
Bed Pressure Drop, psi	5	2	40	5	5	5	15	15
Ignition Spike Pressure, psi	----- not recorded -----							
Ignition Delay msec.	4,500	1,100	900	1,000	1,100	550	120	2,100
Wt. % Catalyst Loss and Fines/Cold Start	----- 0.5 -----							
Pulse Duration, sec.	2	2	15	15	15	5	5	2
Remarks								

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(C) APPENDIX A (Cont'd) (U)
Catalyst No. 428-80
(Esso 202)

Description: 12% Ruthenium, 33%
Cobalt CO-impregnated on
1404-1/8" Alumina

	Run No.									
	1	2	3	4	5	6	7	8	9	10
Fuel Temp., °C					25					
Bed Start-up Temp. °C	25	57	100	25	100	190	117	130	166	25
Bed Inlet Steady Temp. °C	155	50	240	180	240	190	182	240	212	--
Bed Center Steady Temp. °C	155	445	240	815	845	845	915	880	915	--
Bed Inlet Steady Pressure, psig	10	25	97	65	80	98	113	114	120	--
Bed Outlet Steady Pressure, psig	10	25	92	65	72	80	95	100	100	--
Bed Pressure Drop, psi	--	--	5	0	8	18	18	14	20	--
Ignition Spike Pressure, psi	not recorded									
Ignition Delay msec.	4,700	600	250	1,500	200	100	150	150	100	1,500
Wt. % Catalyst Loss and Fines/Cold Start	0.6									
Pulse Duration, sec.	4.5	4.8	4.8	4.9	4.9	4.9	15	15	15	--
Remarks										

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-78
(Esso 205)

Description: 32% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.						
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Fuel Temp., °C	----- 25 -----						
Bed Start-up Temp. °C	25	25	25	40	60	80	100
Bed Inlet Steady Temp. °C	220	210	210	210	215	215	215
Bed Center Steady Temp. °C	900	845	845	845	845	845	840
Bed Inlet Steady Pressure, psig	112	110	110	110	122	117	113
Bed Outlet Steady Pressure, psig	110	110	107	107	112	100	110
Bed Pressure Drop, psi	2	0	3	3	10	17	3
Ignition Spike Pressure, psi	----- not recorded -----						
Ignition Delay msec.	200	100	160	60	20	15	10
Wt. % Catalyst Loss and Fines/Cold Start	----- 1.7 -----						
Pulse Duration, sec.	----- 5 -----						
Remarks	---- Half Bed Used with 1404-1/8" Filler ----						

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-83-A
(Esso 206)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Run No.													
Fuel Temp., °C								25						
Bed Start-up Temp. °C	25	40	60	80	100	100	120	25	25	120	100	80	60	40
Bed Inlet Steady Temp. °C	230	225	225	225	--	230	230	230	240	240	280	945	775	910
Bed Center Steady Temp. °C	880	880	880	845	--	860	860	860	790	790	845	835	815	830
Bed Inlet Steady Pressure, psig	--	98	115	123	--	123	123	135	--	136	145	145	145	145
Bed Outlet Steady Pressure, psig	--	--	100	107	100	100	107	115	138	113	120	120	117	118
Bed Pressure Drop, psi	--	--	15	16	--	23	16	20	--	23	25	25	27	27
Ignition Spike Pressure, psi								not recorded						
Ignition Delay msec.	40	80	80	85	--	75	40	260	340	20	25	45	75	150
Wt. % Catalyst Loss and Fines/Cold Start								0.62						
Pulse Duration, sec.	5	5	5	5	5	5	5	5	1	1	5	5	5	5
Remarks														

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-83-A
(Esso 206)

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Run No.													
	25													
Fuel Temp., °C	60	80	100	120	60	80	100	120	40	60	60	80	40	100
Bed Start-up Temp. °C	915	220	205	205	185	185	180	205	180	--	220	265	205	205
Bed Inlet Steady Temp. °C	790	770	780	775	760	790	790	710	680	--	845	845	840	845
Bed Center Steady Temp. °C	132	132	132	135	125	139	139	123	97	--	118	118	117	125
Bed Inlet Steady Pressure, psig	110	110	110	130	106	113	113	117	90	--	112	112	112	117
Bed Outlet Steady Pressure, psig	22	22	22	5	19	26	26	15	7	--	6	6	5	8
Bed Pressure Drop, psi	not recorded													
Ignition Spike Pressure, psi	85	60	55	45	35	45	45	45	100	35	25	50	130	45
Ignition Delay msec.	0.62													
Wt. % Catalyst Loss and Fines/Cold Start	5	5	5	5	2	5	4.3	4.3	2.5	2.5	2.5	2.5	2.5	2.5
Pulse Duration, sec.														
Remarks														

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(C) APPENDIX A (Cont'd) (U)
Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Fuel Temp., °C														
Bed Start-up Temp. °C	25	80	88	100	25	120	80	127	260	166	85	25	40	60
Bed Inlet Steady Temp. °C	250	250	240	245	250	240	240	245	320	245	240	205	205	205
Bed Center Steady Temp. °C	940	940	940	1000	910	940	1050	930	940	915	850	845	845	845
Bed Inlet Steady Pressure, psig	128	130	130	130	130	130	130	130	130	130	125	123	122	118
Bed Outlet Steady Pressure, psig	118	125	125	128	120	120	123	120	120	120	120	114	114	117
Bed Pressure Drop, psi	10	5	5	2	10	10	7	10	10	10	5	9	8	1
Ignition Spike Pressure, psi	335	335	335	335	335	335	335	335	335	335	350	200	350	350
Ignition Delay msec.	100	45	20	10	22	5	40	5	<5	<5	20	100	65	5

Wt. % Catalyst Loss and Fines/Cold Start
Pulse Duration, sec.
Remarks

(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Run No.													
	25													
Fuel Temp., °C	80	100	25	40	60	80	25	40	60	80	25	25	25	25
Bed Start-up Temp. °C	205	205	205	200	200	190	205	205	200	205	195	190	180	180
Bed Inlet Steady Temp. °C	845	845	845	835	835	835	845	845	845	845	760	760	730	760
Bed Center Steady Temp. °C	125	125	122	115	115	118	125	120	120	112	104	114	108	110
Bed Inlet Steady Pressure, psig	120	120	118	115	115	118	120	114	114	112	104	114	100	110
Bed Outlet Steady Pressure, psig	5	5	4	0	0	0	5	6	6	0	0	0	8	0
Bed Pressure Drop, psi	350	350	350	117	117	117	325	325	325	325	350	180	60	93
Ignition Spike Pressure, psi	<5	<5	220	65	5	<5	200	60	<5	<5	180	100	45	75
Ignition Delay msec.														
Wt. % Catalyst Loss and Fines/Cold Start	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	1.5	1.5	1.5	1.5
Pulse Duration, sec.														
Remarks														

(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.														
	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
Fuel Temp., °C	25														
Bed Start-up Temp. °C	25														
Bed Inlet Steady Temp. °C	180	180	180	180	180	180	170	170	155	155	145	170	145	170	170
Bed Center Steady Temp. °C	760	790	770	850	760	760	770	760	770	815	760	810	275	880	880
Bed Inlet Steady Pressure, psig	106	110	110	113	109	106	106	106	106	119	112	115	106	114	114
Bed Outlet Steady Pressure, psig	106	106	105	107	100	100	100	100	100	112	107	107	95	100	107
Bed Pressure Drop, psi	0	4	5	6	9	6	6	6	6	7	5	8	11	14	7
Ignition Spike Pressure, psi	240	150	255	270	270	75	165	80	240	310	306	310	300	300	320
Ignition Delay msec.	140	105	150	170	150	70	110	80	160	180	160	180	170	150	150
Wt. % Catalyst Loss and Fines/Cold Start															
Pulse Duration, sec.	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Remarks															

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-83-B
(Esso 207)

Description: 23% Ruthenium on
Preformed 1404-1/8"
Alumina

	Run No.														
	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Fuel Temp., °C	25														
Bed Start-up Temp. °C	25														
Bed Inlet Steady Temp. °C	135	170	170	170	170	170	170	145	145	170	170	170	170	170	170
Bed Center Steady Temp. °C	205	205	680	500	205	240	240	425	280	355	205	205	200	200	200
Bed Inlet Steady Pressure, psig	107	110	115	115	115	115	110	100	115	112	130	103	165	165	165
Bed Outlet Steady Pressure, psig	100	105	107	107	107	107	105	95	100	95	95	88	88	88	88
Bed Pressure Drop, psi	7	5	8	8	8	8	5	5	15	17	35	75	77	77	77
Ignition Spike Pressure, psi	180	75	250	325	163	73	119	257	335	120	350	108	0	0	0
Ignition Delay msec.	110	60	110	130	90	60	95	150	190	140	255	70	85	125	140
wt. % Catalyst Loss and Fines/Cold Start															
Pulse Duration, sec.	2.0														
Remarks															

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-82-C
(Esso 208)

Description: 36% Ruthenium on
Alumina

Run No.														
<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>
----- 23 -----														
25	40	60	80	100	25	40	60	80	100	25	40	60	100	80
200	195	195	195	195	195	220	195	184	220	205	205	205	195	205
815	815	815	845	815	815	800	815	815	790	815	815	815	815	815
118	110	110	110	110	120	115	110	110	110	115	115	115	115	115
103	100	97	97	100	107	102	100	100	100	107	100	100	104	104
15	10	13	13	10	13	13	10	10	10	8	15	15	11	11
58	25	18	0	0	150	45	0	0	0	192	40	0	0	0
90	50	40	30	<5	150	70	20	20	5	185	75	50	75	20
----- 0.78% -----														

Wt. % Catalyst Loss and Fines/Cold Start

Remarks

(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-82
(Esso 209)

Description: 33% Ruthenium on
Silica Alumina

	Run No.											
	1	2	3	4	5	6	7	8	9	10	11	12
Fuel Temp., °C	23											
Red Start-up Temp. °C	25	40	60	80	100	25	40	60	80	100	25	40
Bed Inlet Steady Temp. °C	200	195	195	195	195	195	220	195	185	220	205	205
Bed Center Steady Temp. °C	815	815	815	845	815	815	800	815	815	790	815	815
Bed Inlet Steady Pressure, psig	118	110	110	110	110	120	115	110	110	110	115	115
Bed Outlet Steady Pressure psig	103	100	97	97	100	107	102	100	100	100	107	100
Bed Pressure Drop psi	15	10	13	13	10	13	13	10	10	10	8	15
Ignition Spike Pressure psi	58	25	18	0	0	150	45	0	0	0	192	40
Ignition Delay msec	90	50	40	30	<5	150	70	20	20	<5	185	75
Wt. % Catalyst Loss and Fines/Cold Start	0.67											
Remarks	each pulse duration - 2 secs.											

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(C) APPENDIX A (Cont'd) (U)

Catalyst No. 428-82
(Esso 209)

Description: 33% Ruthenium on
Silica Alumina

	Run No.											
	13	14	15	16	17	18	19	20	21	22	23	
Fuel Temp., °C												
Bed Start-up Temp. °C	60	100	80	25	40	60	80	100	25	25	25	
Bed Inlet Steady Temp. °C	205	195	205	205	205	205	205	205	190	195	205	
Bed Center Steady Temp. °C	815	815	815	790	790	790	815	815	790	815	815	
Bed Inlet Steady Pressure, psig	115	115	115	115	107	115	107	115	110	110	117	
Bed Outlet Steady Pressure psig	100	104	104	97	95	97	97	97	100	95	105	
Bed Pressure Drop psi	15	11	11	18	12	18	10	18	10	15	12	
Ignition Spike Pressure psi	0	0	0	350	0	0	0	0	107	72	350	
Ignition Delay msec	50	5	20	175	25	20	7	7	135	110	235	
Wt. % Catalyst Loss and Fines/Cold Start	0.67											
Remarks	each pulse duration - 2 secs.											

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13. ABSTRACT <div style="margin-bottom: 20px;"> (U) This report describes the work conducted during the second quarter of this contract. Our effort, during this period, has been primarily devoted to the investigation of cobalt-ruthenium hybrid catalysts and ruthenium catalysts, both using alumina support structures. </div> <div> (C) The use of ruthenium in cobalt-ruthenium hybrid catalysts effected a significant reduction in catalyst ignition delay when compared with cobalt catalysts containing no ruthenium. However, ruthenium on an alumina support, containing no cobalt, was significantly more active than the cobalt-ruthenium hybrid structures; ignition delay performance of alumina supported ruthenium catalysts approached the performance of Shell 405. </div>		

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